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PRELIMINARY NOTE

Anionic Co-Oligomerisations with Hexafluorobut-2-yne

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SUMMARY

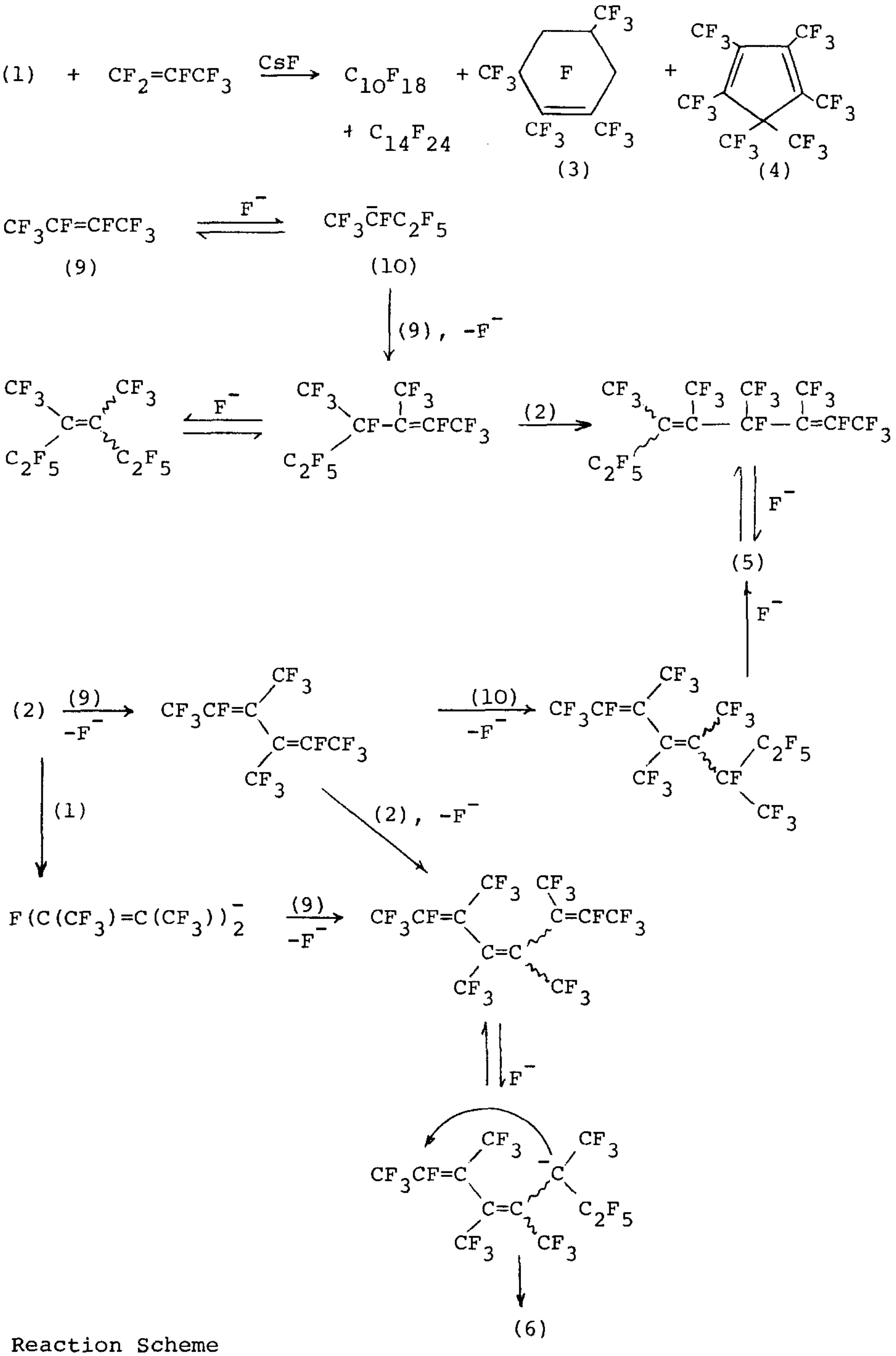
Co-oligomerisations of F-but-2-yne (1) with F-propene, -2-butene, and -cyclopentene have been investigated and some interesting cyclic products have been identified.

It is well established [1] that F-butenyl anions (2) are generated by reaction of fluoride ion with F-2-butyne (1) and these anions have been trapped in various ways [2,3,4].

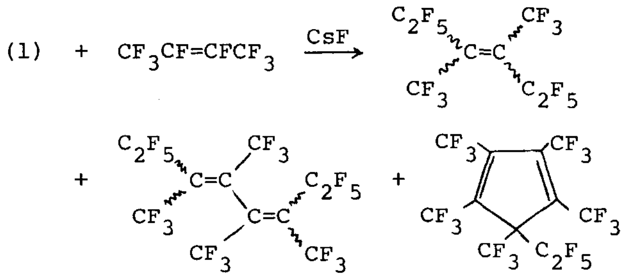
$$F^- + \underset{(1)}{CF_3C{\equiv}CCF_3} \rightleftharpoons \underset{(2)}{CF_3CF{=}\bar{C}CF_3}$$

Further reaction of (2) with F-2-butyne (1) gives a polymer [3,4,5,6] which provides the only reported example of an ionic polymerisation of an unsaturated fluorocarbon. We now report preliminary results on the co-oligomerisation of (1) with F-alkenes and -cycloalkenes, as well as co-polymerisation with dimethylacetylenedicarboxylic ester using CsF in sulpholan.

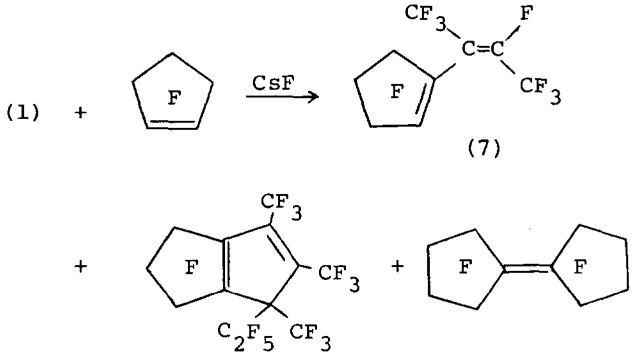
Reactions of (1) with fluorinated alkenes occur readily but products are very dependent on reaction conditions, which have not yet been optimised. Indeed, substantial amounts of oligomeric materials of, so far, uncertain structure are usually formed but the feature of special interest is the formation of cyclic compounds e.g. (3,4,6,8). Reactions between (1) and F-propene, -2-butene, and -cyclopentene have been investigated and compounds identified in the reaction products are indicated below.



Reaction Scheme



(5) (6)

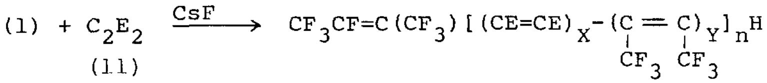


(7)

(8)

These products may be accounted for on the basis of conventional carbanionic processes, as illustrated in the Reaction Scheme for the system involving F-2-butene. Structures of the new compounds (3) - (8) follow simply from analytical, i.r., and ^{19}F n.m.r. data on the isolated compounds. For example, compound (3) shows 2 x CF_2, 2 x $-\overset{|}{\underset{|}{C}}-F$, and 4 x CF_3 (the spectrum indicates a mixture of geometric isomers) and compound (4) shows only CF_3 groups. Other structures follow in a similar way and the configuration of (7) follows from well established J values for cis- and trans-CF_3-F coupling [7].

Like F-2-butyne (1), dimethylacetylenedicarboxylic ester (11) is known to undergo anionic polymerisation with nucleophiles [8,9,10]. Therefore, we have been able to prepare copolymers of the two systems in the presence of fluoride ion. Typically, polymer compositions of (1):(11) = 9:1 - 2:1 have been obtained and the properties of these interesting functional fluoropolymers (12) will be pursued.



$$(1) + \underset{(11)}{C_2E_2} \xrightarrow{CsF} CF_3CF{=}C(CF_3)[(CE{=}CE)_X-(\underset{CF_3}{C}=\underset{CF_3}{C})_Y]_nH$$

E = COOMe (12)

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